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노말언데칸의 연소특성치의 측정

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The Measurement of Combustible Characteristics of n-Undecane

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요 약

노말언데칸의 안전한 취급을 위해서 하부인화점, 상부인화점, 연소점 그리고 발화지연시간에 의한 발화온도를 측정하였다. 또한 노말언데칸의 하부와 상부인화점의 측정값을 이용하여 폭발하한계와 상한계를 예측하였다. 밀폐식 장치에 의한 노말언데칸의 하부인화점은 59 °C와 67 °C로 측정되었고, 개방식 장치에 의한 하부인화점은 67 °C와 72 °C로 측정되었다. 클리브랜브 장치에 의한 노말언데칸의 연소점은 74 °C로 측정되었다. ASTM E659-78 장치를 사용하여 자연발화온도와 발화지연시간을 측정하였고, 여기서 측정된 최소자연발화온도는 198 °C였다. 측정된 하부인화점 59 °C와 상부인화점 83 °C를 이용하여 예측된 폭발하한계는 0.65 Vol.%, 폭발상한계는 2.12 Vol.%였다.

ABSTRACT

For the safe handling of n-undecane, the lower flash points and the upper flash point, fire point, AITs (auto-ignition temperatures) by ignition delay time were experimented. Also lower and upper explosion limits by using measured the lower and upper flash points for n-undecane were calculated. The lower flash points of n-undecane by using closed-cup tester were measured 59 °C and 67 °C. The lower flash points of n-undecane by using open cup tester were measured 67 °C and 72 °C, respectively. The fire point of n-undecane by using Cleveland open cup tester was measured 74 °C. This study measured relationship between the AITs and the ignition delay times by using ASTM E659 apparatus for n-undecane. The experimental AIT of n-undecane was 198 °C. The estimated lower and upper explosion limit by using measured lower flash point 59 °C and upper flash point 83 °C for n-undecane were 0.65 Vol.% and 2.12 Vol.%.

Keywords : n-Undecane, Flash point, Explosion limit, Fire point, Autoignition temperature (AIT)

1. Introduction

The three most common chemical industry accidents are fires, explosions, toxic releases. The combustible solvents are the most common sources of fires and explosions in the chemical plants. The fire and explosion properties necessary for safe storage, transport, process design and handling of flammable substances are lower explosion limits (LEL), upper explosion limits (UEL), flash point, fire point, AIT (auto ignition temperature), MIE (minimum ignition energy), MOC (minimum oxygen concentration) and heats of combustion etc.[1].

The flash point and the fire point are relevant to safety. The flash point is the best known and most widely used flammability property for the evaluation of the flammability hazard of combustible liquids. It is an important criterion for the fire hazard rating of these liquids. A liquid that exhibits a flash point value below ambient temperature, and can thus give rise to flammable mixtures under ambient conditions, is generally considered to be more hazardous than one reflecting a higher flash point. The fire point of a lubricant is the point at which vapors are released rapidly enough to support combustion. The fire point is the temperature of the flammable liquid at which there will be flaming combustion, sustained 5 seconds in response to the pilot flame[2].

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The explosion limit is one of the combustible properties used to determine the fire and explosion hazards of the flammable substances[2]. The explosion limits are used to classify flammable liquids according to their relative flammability. Such a classification is important for the safe handling of flammable liquids which constitute the solvent mixtures. Also, the flash point of a combustible liquid is the temperature at which the vapor pressure of the liquid provides a concentration of the vapor in air that corresponds to the explosion limit.

The autoignition is a phenomena of particular interest to the chemical engineer concerned with safe operation, it involves the occurrence of combustion in the absence of an external ignition sources. The autoignition temperature (AIT) describes the minimum temperature to which a substance must be heated, without the application of a flame or spark, which will cause that substance to ignite. The lower the ignition temperature, the greater the potential for a fire started by typical laboratory equipment[3].

Montemayor et al.[4] have been obtained flash point values for n-decane, n-undecane, n-tetradecane and n-hexadecane for ASTM D92 (Cleveland Open Cup Tester) and ASTM D93 (Pensky-Martens Closed-cup Tester). Ha[5-7] has been obtained flash points and autoignition temperature of n-dodecane, n-tridecane and n-tetradecane by using various combustion test methods.

In this study, we measured flash points, fire points and AIT for n-undecane. Predictive explosion limits of n-undecane based on measured flash point proposed as process safety data. These presented data are typically used as MSDS (Material Safety Data Sheet) update, petroleum tank fire extinguishment index, fire investigation, resemble petroleums distinct etc..

2. Physical and Combustion Characteristics of n-Undecane

2.1 Physical Characteristics of n-Undecane

Several nations provide on MSDS for safety handling, transportation, storage and treatment of hazardous materials using the workplace. A lot of handbooks and articles appear to combustion characteristics of flammable substances. The Physical Characteristics of n-undecane suggested by literatures are summarized in Table 1.

Table 1. Physical Characteristics of n-Undecane

Properties \ Component	n-Undecane
CAS number	1120-21-4
Molecular formula	$CH_3(CH_2)_9CH_3$
Boiling point	196 ^oC
Melting point	−26 ^oC
Density	0.74 g/cm^3
Vapor pressure	0.412 mmHg (25 ^oC)
Viscosity	1.08 Centipoise (25 ^oC)
Solubility(Water)	0.1065 mmg/L (25 ^oC)
Critical temperature	365.65 ^oC
Critical pressure	19.4 atm
Vapor density (Air=1)	5.4
Specific gravity (Water=1)	0.7

2.2 Reaction and Combustible Characteristics of of n-Undecane

n-Undecane is the second oils of the fourth category of hazardous materials in Hazardous Materials Safety Management Act in Korea. Also this material is working environment measurement and harmful material for adminstration in Industrial Safety and Occupational Act. n-Undecane is the colorless liquid. It can not dissolve into water, and it can dissolve into alcohols and ethers. It is main raw material of n-undecane, others applications include: hydraulic oil of large-scale punch, paraffin chloride, anticorrosive paint. powder paint, and top-grade melt adhesive. Also, it is very useful chemical and medical intermediate, it can be used ad curing agent of epoxy material resin, polyester improved additive etc.[9].

The ignition sources of flee condition of n-undecane are heat, flame, spark and other ignition sources. The escape of n-undecane vapor can spread in a moment to ignite from ignition sources because the weight of n-undecane vapor is more than weight of air. The fire extinguishing media of n-undecane use form, dry chemical or carbon dioxide (water may be ineffective).

3. Analysis of Fire and Explosion Characteristics of n-Undecane

In our observation, the AIT and the explosion limits of n-undecane are reported only in the Ignition Handbook. The the lower and uper explosion limits of n-undecane are 0.68 Vol.% and 4.8 Vol.%, respectively. The AIT of n-undecane is reported 202 ^oC in this handbook.

The several authoritative sources (NFPA, Ignition and Sigma) reported the flash points of n-undecane as 60 ^oC. The SAX and Lange reported the flash points of n-unde-

Table 2. The Lower Flash Point of Several Reported Data for n-Undecane

Compound	Flash points [°C]								
	NFPA[10]	Iginition[11]	Sigma[12]	SAX[13]	Lange[14]	Montemayor[4]			
n-Undecane	65	60	60	65 (OC)	65 (OC)	68.7* (PMCC)	65.9* (Seta)	67.1* (TC.C)	73* (COC)

* PMCC: Pensky-Martens closed-cup.
* Seta: Setaflash closed-cup.
* TCC: Tag closed-cup.
* COC: Cleveland open cup.

cane as 65 °C. And Montemayor et al. reported the closed-cup flash point 65.9~67.1 °C, the open cup flash point 73 °C. According to prior articles, the flash points of n-undecane reported from 60 °C to 73 °C. The flash points of n-undecane suggested by literatures are summarized in Table 2.

4. Experimental Apparatus of Combustible Characteristics

4.1 Experimental Material

The n-undecane was purchased from Kanto (Japan), with a minimum purity of 99.0 %. This chemical were used directly without any purification.

4.2 Experimental Apparatus

4.2.1 Flash Point Apparatus

Some of the parameters that affect flash points can be briefly considered tester configuration, ignition sources, temperature control, sample quantity, sample homogeneity, ambient pressure, operator bias etc.[1,2,5,6].

In this study, the components for Pensky-Martens closed-cup, Setaflash closed-cup, Tag open cup and Cleveland open cup testers introduce briefly[5,6]. These testers manufactured by Koehler Instrument Co..

The basic system configuration of Pensky-Martens closed cup tester consist of a test cup, cover and stove. The volume of the test cup is 100 ml and was made of brass. The flange is equipped with devices for locating the position of the test cup in the stove. The cover consists of cover proper, shutter, flame-exposure device, pilot flame and stirring device. Heat is supplied to the cup by means of the stove. The stove consists of an air bath and a top plate.

The Setaflash closed cup tester consist of a sample cup, time controller, test flame device, thermometer and temperature controller. The Setaflash closed cup tester is operated according to the standard test method, ASTM D 3278.

The basic system configuration of the Tag open cup tester consist of a sample cup, water bath, test flame device, level gauge, electrical heater, overflow path, thermometer and temperature controller. The pure components is added by mass and the sample cup (70 ml) was filled with the mixture.

Determines flash and fire points by the Cleveland open-cup method. Consists of test flame applicator, brass test cup, thermometer support, heating plate and electric heater. Applicator is precisely aligned per specifications and pivots for the test flame application at specified temperature intervals. Hinged thermometer support raises to facilitate placement and removal of test cup. Adjust flame size using built-in needle valve and comparison bead.

Some of the parameters of the standard flash point test methods are summarized in Table 3[5-7].

Table 3. Comparison of Several Flash Point Test Methods

Test methods	Test vessel diameter (cm)	Test vessel depth (cm)	Test vessel volume (ml)	Heating methods
ASTM D93 Pensky-Martens closed-cup	5.085	5.6	100	For ordinary liquids, the temperature of the specimen is increased at 5~6 °C/min
ASTM D3278 Setaflash closed-cup	5.0	1.0	2 or 4	Sample cup is electrically heated or chilled and sample temperature is kept constant
ASTM D1310 Tag open cup	5.3	5.0	70	The temperature of the specimen is increased at 1±0.25 °C/min.
ASTM D92 Cleveland open cup	6.4	3.4	80	The temperature of the specimen is increased at 5~6 °C/min

4.2.2 Autoignition Temperature Apparatus (ASTM E659)

This test method of the auto ignition temperature (AIT) covers the determination of hot flame and cool flame autoignition temperatures of a liquid chemical in air at atmospheric pressure in a uniformly heated vessel. AIT tests are conducted according to ASTM E659 (Standard Test Method for Auto-ignition Temperature of Liquid Chemicals). This tester consists of furnace, temperature controller, thermocouple, test flask, hypodermic syringe, mirror, and air gun.

The test procedure employs a 500 ml flask that is uniformly heated in a special purpose furnace. A fine thermocouple in the flask is used to monitor temperature changes that occur upon injection of a small quantity (0.1 ml) of fuel into the flask. The test temperature is progressively lowered until ignition does not occur within 10 minutes at any fuel concentration[5-7].

5. Results and Investigations

5.1 Prediction of Lower Explosion Limit by Means of Measured Flash Point and Fire Point

The open cup (OC) flash points are generally somewhat higher than the closed-cup (CC) flash points for same materials.

Special precautions should be taken when the product has a low flash point. Materials that have a low flash point are a greater fire hazard than materials having a high flash point. From the definition of flash point, the flash point of a flammable liquid is defined as that temperature at which the vapor pressure of the specified liquid is such as to produce a concentration of vapor in the air that corresponds to the lower flammable limit.

In this study, the flash point of n-undecane measured by Pensky-Martens closed-cup, Setaflash closed-cup, Tag open cup and Cleveland open cup testers. The fire point of n-undecane measured by using Tag open cup and Cleveland open cup testers.

The explosion limits of n-undecane predicted by using the measured flash points and fire points. An equation for the saturated vapor pressure, P^f, is needed to estimate the explosion limits. One of the most common correlation is the Antoine equation[15]:

$$\log P_i^2 = 7.8832 - \frac{2250.79}{(t+254.149)} \quad (1)$$

where, P^f is saturated vapor pressure (mmHg), t is flash point temperature (°C).

In this study, it is summarized estimated explosion limits values by equation (1) with experimental flash points and fire point by using four testers for n-undecane in Table 4. The calculated lower explosion limit by flash point 59 °C of Setaflash tester for n-undecane was about 0.65 Vol.%. And the calculated upper explosion limit by flash point 83 °C of Setaflash tester was about 2.12 Vol.%. The proposed

Table 4. Comparison of Estimated Explosion Limits by Experimental Flash Points and Fire Point for n-Undecane

Testers	Experimental (°C)			Estimated (EL) (Vol.%)		
	Lower flash points	Upper flash points	Fire points	by Lower flash points	by Upper flash points	by Fire points
Setaflash	59	83	-	0.65	2.12	-
Pensky-Martens	67	-	-	0.99	-	-
Tag	67	-	-	0.99	-	-
Cleveland	72	-	74	1.26	-	1.4

Table 5. Comparison of Lower Flash Points of Several References for n-Undecane

Compounds \ References	NFPA[10]	SFPE[16]	Sigma[16]	Affens[17]	Montemayor et al.[4]
n-Hexane	−22 °C	−22 °C	−23.3 °C	-	-
n-Hepatne	−4 °C	−4 °C	−1.1 °C	−1 °C	-
n-Octane	13 °C	13 °C	15.5 °C	15 °C	-
n-Nonane	31 °C	31 °C	32.8 °C	33 °C	-
n-Decane	46 °C	44 °C	46.1 °C	48 °C	52.8 °C
n-Undecane	65 °C (OC)	65 °C (OC)	60 °C	64 °C (C.C.)	67.1 °C (TCC) 68.7 °C (PMCC)

lower explosion limit can use efficiently in the fire and explosion protection equipment.

5.2 Property Investigation of Measured Flash Point

The flash points of n-undecane are scarcely literatures but in the industrially important material. In order to review validity of measured flash points for n-undecane, we compare with several sources (NFPA, SFPE, Sigma, Affens and Montemayor) in Table 5.

Also, in order to investigate validity of flash points for n-undecane, we are plotted from n-hexane flash point to n-undecane flash point of NFPA literature and measured flash points for n-undecane in Figure 1.

In plotting results, the flash point of n-undecane which proposed this study is similar trend the flash points of several established literatures. Therefore, the measured flash points for n-undecane in this study has appropriated.

In the Figure 1, the trend of flash point of n-undecane is beside the point from the flash points of NFPA literature because flash point of n-undecane measured the open cup (O.C.) tester.

5.3 Investigation of Autoignition Temperature of n-Undecane

It is understood that autoignition means the ignition of combustible matter in air subjected to uniform heat. The temperature of the surrounding atmosphere (storage temperature) which initiates autoignition after self-heating of the product is called the AIT. The AIT describes the minimum temperature to which a substance must be heated, without the application of a flame or spark, which will cause that substance to ignite.

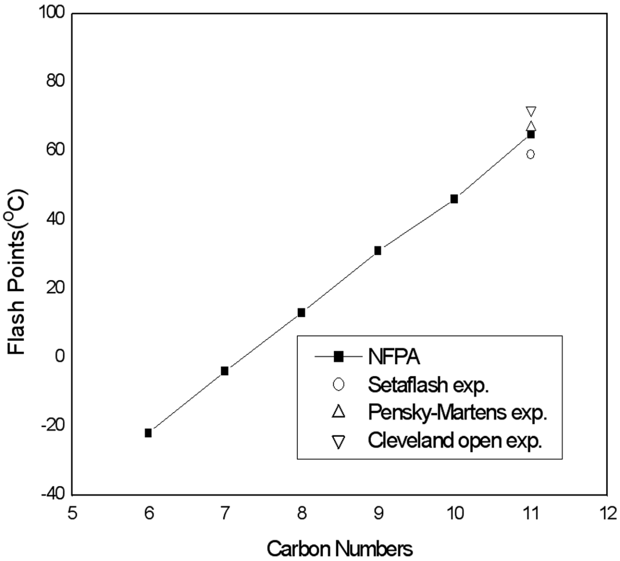

Figure 1. Comparison of the flash points between NFPA and experimental data.

The measurement AIT is dependent upon many factors, namely, ignition delay, ambient pressure, configuration, fuel/air stoichiometry, oxygen concentration, vessel size, flow condition, initial temperature, catalytic material, impurity etc.[1,2,,5,6].

We have searched the several handbooks and references in order to investigate validity the measured AIT for n-undecane. But the AIT for n-undecane are reported in Ignition handbook 202 °C. Therefore, we proposed experimental data which obtained in this study.

In this study, the initial temperature of autoignition for n-undecane set up to 200 °C based on the AIT of hydrocarbon compounds. The n-undecane ignited in this temperature and ignition delay time was 88.07 second. therefore, when temperature of autoignition set up to 170 °C, a low 30 °C. The n-undecane do not ignited. We are found AIT 198 °C to turn down 1~2 °C based on 170 °C. The ignition delay time of AIT 207 °C is ignited 101.77 second. And the ignition delay time of the ignition temperature 280 °C to turn up 5~10 °C based on the AIT 198 °C was 1.98 second.

The relationship between the ignition temperature and the ignition delay time for n-undecane are summarized in Table 5.

In the case of most combustible materials. the relationship between the ignition temperature and the ignition delay time may be approximated within finite limits by the equation

$$\ln\tau = A + B\left(\frac{1}{T}\right) \tag{2}$$

where τ is the ignition delay time, T is the ignition temperature, and A and B are constant.

The coefficients of optimized equation by regression analysis is following.

$$\ln\tau = -23.16 + 13046.84\left(\frac{1}{T}\right) \tag{3}$$

The equation (3) are presented in equation (4) by the relationship between $\log\tau$ and (1/T).

$$\log\tau = -10.06 + 5666.38\left(\frac{1}{T}\right) \tag{4}$$

The comparison of experimental and calculated ignition delay time by the AIT for n-undecane are illustrated Table 6 and Figure 2.

It is another index, replacing A.A.P.E. in situation when an accurate quantitative comparison between the reported value and estimated value are attempted. The average abso-

Table 6. Comparison of Experimental and Calculated Ignition Delay Time by the AIT for n-Undecane

No.	T [K]	$\tau_{exp.}$ [s]	$\ln\tau_{exp.}$	$\tau_{est.}$ (Eq. 3)
1	471	101.77	4.62272	92.73
2	473	88.07	4.47813	82.49
3	483	51.90	3.94932	46.62
4	493	24.54	3.20030	26.96
5	503	13.65	2.61374	15.94
6	513	9.00	2.19722	9.61
7	523	5.12	1.63315	5.91
8	533	3.46	1.24127	3.70
9	543	2.37	0.86289	2.36
10	553	1.98	0.68310	1.53
A.A.D.	-	-	-	2.67

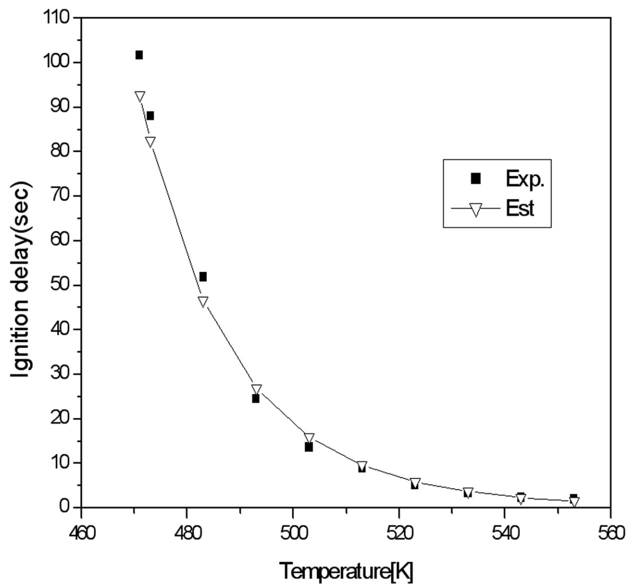

Figure 2. A comparison between the experimental and calculated delay times for n-undecane.

lute deviations (A.A.D.)[5-7] is :

$$\text{A.A.D.}=\sum\frac{|\tau_{est.}-\tau_{exp.}|}{N} \quad (5)$$

where the A.A.D. is a measure of agreement between the experimental data and the calculated values.

The predicted ignition delay times by Equation (3) are in agreement with the experimental ignition delay times, and A.A.D. (Average Absolute Deviation) is 2.67 second and the coefficient of determination (r^2) is 0.99.

In the high temperature regime, the effective activation energy is 50 to 90 kJ/mol, while in the low temperature region values 140 to 190 kJ/mol[9]. The activation energy can calculate by using Semenov equation[19]. Semenov related several variables by the equation

$$\log\tau=\frac{52.55E}{T}+B \quad (6)$$

where τ is ignition delay (s), E is activation energy (kJ/mol) and B is constant.

The calculated activation energy by the relationship between equation (4) and equation (6) is 107.83 kJ/mol.

6. Conclusions

For the safe handling of n-undecane, the lower flash points, the upper flash point, fire point and AITs (auto-ignition temperatures) by ignition delay time were experimented. And predictive explosion limits based on measured flash point proposed as process safety data.

(1) The lower flash points of n-undecane by using closed-cup tester were experimented 59~67 ^{o}C. The lower flash points of n-undecane by using open cup tester were measured 67~71 ^{o}C.

(2) The fire point of n-undecane by using Cleveland open cup were measured 74 ^{o}C.

(3) The upper flash points of n-undecane by using Setaflash closed-cup tester was measured 83 ^{o}C.

(4) The calculated lower and upper explosion limit by using measured lower 59 ^{o}C and upper flash point 83 ^{o}C for n-undecane were 0.65 Vol.% and 2.21 Vol.%.

(5) The experimental AIT of n-undecane was 198 ^{o}C.

(6) The activation energy value for n-undecane was 107.82 kJ/mol.

(7) The coefficients of optimized equation between ignition temperature and ignition delay time is following.

$$\log\tau=-10.06+5666.38\left(\frac{1}{T}\right)$$

References

1. F. P. Lees, "Loss Prevention in the Process Industries", Vol. 2, 2nd ed., Butterworth-Heinemann (1996).
2. D. Drysdale, "An Introduction to Fire Dynamics", 2nd ed., John Wiley and Sons (1998).
3. D. A. Crowl and J. F. Louvar, "Chemical Process Safety: Fundamental with Applications", 2nd ed., Pearson Education Inc. (2002).
4. R. E. Montemayor, J. E. Rogerson, J. C. Colbert and S. B. Schiller, "Reference Verification Fluids for Flash Point Determination", Journal of Testing and Evaluation, Vol. 27, No. 6, pp. 423-427 (1999).

5. D. M. Ha, “The Investigation of Combustible Hazard by Measurement of Flash Point and Auto-ignition Temperature of n-Dodecane”, Journal of the Korean Institute of Fire Science & Engineering, Vol. 25, No. 2, pp. 120-125 (2011).
6. D. M. Ha, “The Investigation of Compatibility of Combustible Characteristics for n-Tridecane”, Journal of the Korean Society of Safety, Vol. 27, No. 3, pp. 83-88 (2012).
7. D. M. Ha, “The Evaluation of Hazard by Measurement of Combustible Characteristics for n-Tetradecane”, Journal of the Korean Society of Safety, Vol. 27, No. 5, pp. 70-76 (2012).
8. D. R. Lide, “CRC Handbook of Chemistry and Physics”, 75th ed., CRC Press (1994).
9. E. Meyer, “Chemistry of Hazardous Materials, 2nd ed.”, Prentice-Hall (1990).
10. NFPA, “Fire Hazard Properties of Flammable Liquid, Gases, and Volatile Solids”, NFPA 325M, NFPA (1991).
11. V. Babrauskas, “Ignition Handbook”, Fire Science Publishers, SFPE (2003).
12. R. E Lenga and K. L. Votoupal, “The Sigma Aldrich Library of Regulatory and Safety ata, Volume ~”, Sigma Chemical Company and Aldrich Chemical Company Inc. (1993).
13. R. J. Lewis, “SAX’s Dangerous Properties of Industrial Materials”, 11th ed., John Wiley & Son, Inc., New Jersey (2004).
14. J. A. Dean, “Lange’s Handbook of Chemistry”, 14th Ed. McGraw-Hill (1992).
15. J. Gmehing, U. Onken and W. Arlt, “Vapor-Liquid Equilibrium Data Collection”, DECHEMA (1980).
16. SFPE, “SFPE Handbook of Fire Protection Engineering”, 2nd ed., SFPE (1995).
17. W. A. Affens and G. W. McLaren, “Flammability Properties of Hydrocarbon Solutions in Air”, Journal of Chemical and Engineering Data, Vol. 17, No. 4, pp. 482-488 (1972).
18. N. N. Semenov, “Some Problems in Chemical Kinetics and Reactivity, Vol. 2”, Princeton University Press, Princeton, N.J. (1959).